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70-76-1011MODELLING OF THE DEFECT STRUCTURE OF β -NiAlGuillermo Bozzolo⁽¹⁾, Carlos Amador⁽²⁾, John Ferrante⁽³⁾ and Ronald D. Noebe⁽³⁾⁽¹⁾Analex Corporation, 3001 Aerospace Parkway, Brook Park, OH 44142-1003⁽²⁾Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 Distrito Federal, México⁽³⁾National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135.Introduction

Major advances in developing the next generation high-temperature, high pressure turbine blades and vanes will be accomplished by coordinated efforts involving innovative component design and advanced materials and processing. Furthermore, the greatest gains in performance will arise through revolutionary changes in materials as opposed to evolutionary and incremental improvements in the properties of current materials. The primary objectives are to reduce blade cooling flow while increasing use temperature and at the same time reduce overall engine weight. This will be accomplished through novel component designs and the replacement of Ni-based superalloys with ordered intermetallic NiAl alloys (1). However, the current materials development approach, no matter how successful, has been strictly empirical. The advancement and implementation of theoretical alloy design procedures would significantly decrease the time and expense for screening various alloy compositions. Consequently, with this much larger goal in mind, this paper contributes to the improvement and testing of one such analytical technique and at the same time provides additional insight to the structure of ordered alloys.

This work concentrates on the β -phase of the Ni-Al system, which exists over a range of stoichiometry from 45-60 at. % Ni (2). At the stoichiometric composition NiAl

should exist in a perfectly ordered state where the Ni atoms occupy the cube corners and the Al atoms occupy the cube centers of a generalized body-centered cubic lattice. Ni-rich alloys are characterized by antisite point defects, where Ni atoms occupy sites in the Al sublattice, resulting in a decrease in lattice parameter and an increase in density with increasing Ni content. A different behavior is observed on the Al-rich side of stoichiometry. There is a steep decrease in lattice parameter as well as a greater than expected decrease in density with increasing Al content. The presence of vacancies in Ni sites would explain such behavior (2-6). Recent X-ray diffraction experiments (7) suggest a richer structure: the evidence, while strongly favoring the presence of vacancies in Ni sites, also suggests the possibility of some vacancies in Al sites in a 3:1 ratio. Moreover, local ordering of vacant sites may be preferred over a random distribution of individual point defects (4).

We apply the recently developed BFS semiempirical method for alloys (8-14) to model non-stoichiometric β -NiAl at zero temperature, in order to provide theoretical support to the current understanding of the defect arrangement in such alloys. A more ambitious project, that of the study of ternary additions to Ni-Al alloys and their effect on properties, could only be attempted once the basic Ni-Al system is adequately described by this theoretical tool in light of the current experimental evidence. This calculation differs from previous BFS studies in that first-principles theoretical input was used instead of experimentally determined properties.

The BFS method

The BFS method has been successfully applied to a variety of situations ranging from segregation profiles (8), alloy structure (9), surface alloying of immiscible metals (10), to numerical simulations of scanning tunneling microscopy (11) and alloy design (12). Two of the characteristics of the BFS method, the minimal need of experimentally determined input data and maximal reliance on the pure constituent properties (13), initially imposed a limitation when dealing with systems like β -NiAl, where both constituents are fcc elements but the alloy is bcc-based. No appropriate experimental input for bcc-Ni and Al is available therefore, for the first time, we will rely on pure first-principles determined input, thus freeing BFS from limitations imposed by availability of experimental data. We also avoid the potential problem of inconsistency and ambiguity in data obtained from different experimental techniques (14).

The BFS method is based on the idea that the energy of formation of an alloy is the superposition of individual contributions ϵ_i of non-equivalent atoms in the alloy (9):

$$\epsilon_i = \epsilon_i^S + g_i(\epsilon_i^C - \epsilon_i^{C_0}). \quad (1)$$

ϵ_i has two components: a *strain* energy ϵ^S , computed with equivalent crystal theory (ECT) (15), that accounts for the actual geometrical distribution of the atoms surrounding atom i , computed as if all its neighbors were of the same atomic species, and a

chemical energy $\varepsilon^C - \varepsilon^{C_0}$, which takes into account the fact that some of the neighbors of atom i may be of a different chemical species. For ε_i^C we interpret the chemical composition as a defect of an otherwise pure crystal. We represent this defect by ‘perturbing’ the electronic density in the overlap region between dissimilar atoms and locating them at equilibrium lattice sites of atom i . The ideas of ECT (15) are used to develop a procedure for the evaluation of the energy associated with this ‘defect’. To free the chemical energy of structural defect energy, which should only be included in the strain energy, we reference ε_i^C to a similar contribution where no such perturbation is included ($\varepsilon_i^{C_0}$). The coupling function g_i , which ensures the correct asymptotic behavior of the chemical energy, is defined as $g_i = e^{-a_i^S}$, where a_i^S is a solution of $\varepsilon_i^S = -E_C^i \left[1 - (1 + a_i^S) \exp(-a_i^S) \right]$ (see ref. 16), and where E_C^i is the cohesive energy for atom i . In the context of BFS, the terms ‘strain’ and ‘chemical’ represent quite different effects than the usually assigned meanings. For a better understanding of this work, we direct the reader to ref. 13 for a detailed description of the calculation of the strain and chemical energy contributions. Except for two parameters determined by fitting to experimental or theoretical alloy properties, the method relies on pure element properties. However, as mentioned above, a difficulty arises when dealing with alloys where the lattice structure differs from that of the ground state single crystals of each component. As originally formulated, the simplicity of BFS relies mostly on the straightforward mixing of the constituents without any phase change between the individual components and the alloy. In our previous work on γ' -Ni₃Al alloys, this condition is satisfied and therefore fcc-based BFS parameters Δ_{AlNi} and Δ_{NiAl} were successfully used for the determination of the surface structure of such alloys (14). That is not the case in this work, and new parameters are therefore needed. For the BFS strain energy calculation, which describes the change in lattice parameter between the components and the β -NiAl alloy, we need the cohesive energy, equilibrium lattice parameter and bulk modulus for each hypothetical bcc-based element, as well as the vacancy formation energy for fitting the ECT parameter α . The BFS chemical energy requires two alloy properties for fitting the BFS interaction parameters Δ_{AlNi} and Δ_{NiAl} .

The parameters needed by the BFS method, including the ECT parameters p , l , λ and α (see ref. 15), were calculated using the Linear Muffin-Tin Orbitals (LMTO) method (17) in the Atomic Sphere Approximation (ASA). This set of parameters, as well as the vacancy formation energy needed for the determination of the parameter α (15), also includes the cohesive energy, lattice parameter and bulk modulus of the hypothetical bcc-based Al and Ni, which are accurately described by the Local Density Approximation (18).

The LMTO is a first-principles based method, the only input information needed being the Bravais lattice and the atomic number of the constituent elements. Details of the first-principles calculations are as follows. The orbital basis used includes s , p ,

LMTO results				
Atom	Lattice Parameter (Å)	Cohesive Energy (eV)	Bulk Modulus (GPa)	Vacancy Energy (eV)
Ni	2.752	5.869	249	3.0
Al	3.190	3.942	78	1.8
ECT parameters				
Atom	p	α (Å ⁻¹)	λ (Å)	l (Å)
Ni	6	3.067	0.763	0.2717
Al	4	1.8756	1.038	0.3695

Table 1: LMTO results and ECT parameters for bcc-based Ni and Al

and d electrons. For the bulk elements the atomic spheres were of equal size. Spheres of the same size were also used for the vacancy calculation. An empty sphere was placed in the site of the removed atom. For the alloy calculation the spheres for the two different atoms were selected to minimize the charge transfer. The number of equivalent irreducible k -points considered were 84 for all structures. Scalar relativistic corrections and the so-called combined corrections were included.

While the parameters of the equation of state are given by a calculation of the bulk crystal, the calculation of the vacancy energy is more involved and requires the use of the supercell method. Sixteen site supercells containing one empty site were constructed, and the energy difference between this and the bulk crystal (sixteen atom unit cell) was taken as the vacancy formation energy. The results of these calculations for the pure elements are quoted in Table 1. The two parameters that the BFS method needs for the alloy can be chosen in several ways. Here we have calculated the formation energy of the B2 (stoichiometric β -NiAl) structure and its equilibrium lattice parameter. The equilibrium lattice parameter determined for β -NiAl is $a_{LMTO} = 2.85$ Å, and the formation energy of the ground state B2 structure is $\delta h = -0.6092$ eV/atom. The BFS parameters thus obtained are $\Delta_{AlNi} = 0.0840$ Å⁻¹ and $\Delta_{NiAl} = -0.0581$ Å⁻¹.

Results and Discussion

The BFS calculation was done on a 72 atoms cell, allowing for atomic relaxation induced by the presence of vacancies and substitutional atoms. Instead of searching for an absolute energy minimum for a given number of Ni and Al atoms located in available lattice sites, we chose to construct a large number of ‘candidate’ distributions

to obtain information on the energetics of the system close to the ground state. These configurations are, to a certain extent, arbitrary, and do not necessarily correspond to the ground state for a given composition. While most are experimentally inaccessible, they serve the purpose of determining trends in the bulk properties of the actual alloys, as seen in Fig. 1. Moreover, if the set of configurations sampled is sufficiently large and the structures are chosen respecting the symmetries that characterize the system, one would expect to find the ground state, or states sufficiently close to it, for each composition. In order to concentrate on the focus of this paper, we leave the details on this computer simulation approach and the atomic distribution for each candidate state for a forthcoming publication. Here, it suffices to say that these configurations include combinations of Ni and Al antisite defects as well as Ni and Al vacancies.

Fig. 1 displays the lattice parameter as a function of Ni concentration for the set of ‘candidate’ configurations from which the lowest energy states are selected for comparison with experiment. Each point corresponds to a distinct arrangement of Ni and Al atoms as well as vacant Ni or Al sites in the calculational cell. We focus our attention on three particular regimes that can be seen in Fig. 1: an inverted V-shaped set of filled symbols with its apex at the stoichiometric composition, a line of circles indicating structures with increasing lattice parameter with increasing Al content, and a large number of configurations enclosed by the boundary line consisting of filled symbols. The configurations denoted by closed symbols represent the lowest energy configurations at each composition. The ascending line of circles corresponds to configurations where no vacancies are present and increasing numbers of Al atoms occupy Ni sites, a typical substitutional defect structure. While substitutional states have the lowest energy for each concentration in the Ni-rich side, the opposite is true for the 45-50 at. % Ni concentration range. The cluster of points enclosed by the inverted V-shaped boundary correspond to configurations characterized by random distributions of vacancies in Al or Ni sites as well as random exchanges of Ni and Al atoms from their equilibrium stoichiometric locations. Stoichiometric β -NiAl is notated by an asterisk.

A comparison of the modeled results with experimental data is displayed in Fig. 2. The theoretical results, shown as a continuous line, consist of the calculated lattice parameter and density for the lowest energy configuration for each composition. The results for Ni-rich alloys, for the minimum energy configurations, show an amazing agreement between theory and experiment (Fig. 2). The linear regime in the density (Fig. 2.a) and lattice parameter (Fig. 2.b) vs. Ni concentration for the range 50-60 at. % Ni is almost exactly reproduced by our calculation. A recent review paper by Noebe et al. (19) provides a convenient linear adjustment of the available experimental results, both for the lattice parameter and density vs. Ni concentration. To highlight the agreement between theory and experiment, we therefore compare those expressions with ones corresponding to the BFS+LMTO results. For comparison purposes, both quantities were normalized to the stoichiometric NiAl values, as there is a slight difference of 1.2 % between the

experimental (2.887 Å) and LMTO values (2.85 Å) for the lattice parameter of the stoichiometric B2 NiAl structure. The expressions for experimental and theoretical results are respectively,

$$\begin{aligned}\left(\frac{\rho}{\rho_0}\right)_{Exp.} &= 0.5339 + 0.009322x_{Ni} \\ \left(\frac{\rho}{\rho_0}\right)_{Th.} &= 0.5324 + 0.009352x_{Ni}\end{aligned}\quad (2)$$

and

$$\begin{aligned}\left(\frac{a}{a_0}\right)_{Exp.} &= 1.0384 - 0.0007914x_{Ni} \\ \left(\frac{a}{a_0}\right)_{Th.} &= 1.0396 - 0.0007689x_{Ni}\end{aligned}\quad (3)$$

for $x_{Ni} = 50 - 60$ at. % Ni.

On the Al-rich side of stoichiometry a more complicated structure is observed. The lowest energy states on the Al-rich side correspond to arrangements of vacancies with no change in site occupancy for the Ni and Al atoms with respect to their original sublattice in NiAl. In the lowest energy configurations, the Ni vacant sites are at next-nearest neighbor distance from each other. Once again, the ensuing values for the lattice parameter and the density as a function of Ni concentration (closed triangles in Fig. 1) can be described by linear relationships and compared to the experimental values (19):

$$\begin{aligned}\left(\frac{\rho}{\rho_0}\right)_{Exp.} &= 0.02x_{Ni} \\ \left(\frac{\rho}{\rho_0}\right)_{Th.} &= 0.19914 + 0.01602x_{Ni}\end{aligned}\quad (4)$$

and

$$\begin{aligned}\left(\frac{a}{a_0}\right)_{Exp.} &= 0.924148 + 0.001517x_{Ni} \\ \left(\frac{a}{a_0}\right)_{Th.} &= 0.840261 + 0.003184x_{Ni}\end{aligned}\quad (5)$$

for $x_{Ni} = 45 - 50$ at. % Ni.

While not directly apparent from Fig. 1, this work also showed that locally ordered arrangements of defects were energetically preferred to random distributions of point defects. For example, at 47.82 at. % Ni in Fig. 1 there are an open and closed triangle of very similar lattice parameter. The difference in these points is that the input structure

of the lowest energy configuration (solid triangle) was composed of a greater degree of ordering of Ni-vacancies. While overall structures composed of Ni-vacancies had the lowest energy at a given composition, a similar trend of lower energy with increasing ordering of point defects was observed within the other types of defect arrangements as well. For example, within the family of configurations composed of Al-vacancies plus Ni-vacancies, the points (hexagons) with lattice parameters closest to those of the ground state consisted of locally ordered arrangements of vacancies (i.e. an Al vacancy shared by two Ni-vacancies at the nearest neighbor distance) while those points further away consisted of more random distributions of point defects. This also hints at the possibility that the actual defect arrangements on the Al-rich side of stoichiometry may be more complicated than normally assumed. A complete treatment of temperature and local relaxation effects would be necessary to absolutely rule out these more complicated structures. But even that would not rule out the possibility that these structures may actually be observed as metastable states since their energy is not that different from defect structures composed solely of Ni-vacancies.

In conclusion, our theoretical modelling of the defect structure of β -NiAl alloys strongly supports the conclusions drawn from experimental evidence indicating that the presence of vacancies is responsible for the sharp decrease in lattice parameter with increasing Al content in non-stoichiometric NiAl alloys. Moreover, the results hint to the possibility that a more complex defect structure exists: the presence of vacancies both in the Ni and Al sublattice and a preference for clustering or local ordering instead of a random distribution of point defects. A second point made in this paper relates to the convenience of combining first-principles results and semiempirical methods for a simple and straightforward analysis of situations that cannot be treated in a similar fashion by each individual technique. Large computational cells for first-principles calculations would impose severe limitations in the number and complexity of the configurations to be considered and the lack of appropriate input data for the semiempirical technique used in the simulation would make it unreliable if not useless. The present results raise confidence in combining these methods for complex applications.

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